

Report for 2004AK21B: Short- and Long-term As-Aluminium Oxyhydroxide Sorption Interactions in Aquatic and Soil Environments

- Conference Proceedings:
 - Tanwar, K.; Trivedi, P.; Schiewer, S.: A multi-scale assessment of As(V)-aluminium oxyhydroxide interactions. 2005. In: Proceedings of ASCE EWRI World Water & Environmental Resources Congress, Anchorage, AK, May 15-19 (12 pp.).
- Other Publications:
 - Tanwar, K.; Schiewer, S.; Trivedi, P.: A multi-scale assessment of As(V)-aluminium oxyhydroxide interactions. 2005. In: Abstracts of ASCE EWRI World Water & Environmental Resources Congress, Anchorage, AK, May 15-19.
 - Tanwar, K.; Trivedi, P.; Schiewer, S.; Pandya, K.: Long-term kinetics of As(V)-aluminum oxyhydroxides interactions: complementing macroscopic results with spectroscopic analyses. 2004. In: Advances in environmental reaction kinetics and thermodynamics: long-term fate of anthropogenic contaminants. Abstracts of the 228th Annual Meeting, American Chemical Society (ACS), Philadelphia, August 22-26.

Report Follows

Problem and research objectives

Arsenic has emerged as a major threat to global sustainability during the last decade. In aquatic and soil environments, arsenic results from natural weathering of minerals as well as from anthropogenic activities, such as mining and wood preservation. In most natural systems, arsenate (As(V)) is the predominant form of As from all of these sources. However, in reducing conditions, arsenic is present in reduced forms, such as arsenite.

Arsenic exposure to human beings can result in acute and chronic health effects such as cancer. Based on recommendations from several ecotoxicological and risk assessment studies, U.S. EPA announced lowering the maximum contaminant level (MCL) for As in drinking water to 10 ppb effective 2006. This new stringent standard emphasizes the need to improve the capability of current environmental models to accurately predict the long term mobility and bioavailability of As in aqueous and soil ecosystems. Therefore, the understanding of As speciation is very critical for accurate risk assessment.

The objective of this research was to study As(V) sorption onto hydrous aluminum oxides (HAO) under traditional boundary conditions as well as continuous As(V) influx conditions. Furthermore, As(V)-HAO interactions were also studied in presence of phosphate to study the effect of oxyanions on As(V) sorption. For this purpose, macroscopic studies were conducted and modeled after determining parameters, such as equilibrium constant (K) and maximum sorption capacity (C_i). However, to predict the long term fate of As(V) in nature, a molecular scale understanding of its interactions with environmentally relevant sorbents is necessary. Therefore, to elucidate the fundamental reaction mechanism at the oxide surface, macroscopic studies are complemented with XAS.

Methodology

All experiments used American Chemical Society (ACS) reagent grade chemicals and double-deionized water. Experiments were performed at 25°C, under closed system conditions (N_2 glove box) to avoid interference from reactive gases, such as carbon dioxide (CO_2) and methane (CH_4). Turbulent hydraulic conditions ($Re \geq 10^5$, with respect to length of reactor) were used to minimize external mass-transfer resistances (Fogler, 2002).

Synthesis and Characterization of HAO

HAO was precipitated according to a modified method of Gadde and Laitinen (1974) (Trivedi and Axe, 1999). Prior to sorption studies, all HAO suspensions were repeatedly centrifuged and washed with double deionized water and then finally aged for 24 h at an adjusted ionic strength (I.S.) of 10^{-2} M $NaNO_3$.

Sorption Studies

All As(V)-HAO sorption studies were conducted using 1 g L^{-1} HAO suspension, at pH 4.5 ± 0.2 , and background I.S. 10^{-2} M $NaNO_3$. The stock solution of As(V) was prepared using sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$) and stored at pH 4.5 in a nitrogen glove box. All arsenate sorption studies were conducted in 1-L HDPE containers, where the bulk aqueous pH was monitored and maintained using a Brinkmann autotitrator (799 GPT Titrino). Preliminary kinetic studies suggested that a contact time of 4 h is sufficient for equilibration of As(V) sorption on the

external surface of HAO. As a result, all isotherm studies were conducted using a reaction time of 4 h for a concentration range of 5×10^{-6} - 5×10^{-3} M of As(V). The effect of competing oxyanions on the sorption of As(V) was studied by allowing equimolar amounts of arsenate and phosphate to react with HAO.

Long-term kinetics of As(V)-HAO interactions were conducted under two different sets of boundary conditions. In the first set, traditional boundary conditions (TBC) were employed, where 10^{-3} M of As(V) was initially added to the HAO suspension and the sorptive uptake was measured as a function of reaction time up to 360 h. Under these conditions, the concentration gradient, which is the primary driving force for the sorption reactions, quickly decreases with time. Continuous influx condition (CIC) experiments were also conducted. In these experiments, a continuous driving force was maintained by adding 10^{-5} M As(V) every 4 h using a dual probe autotitrator (Brinkmann 799 GPT Titrino), which also monitored and maintained the system pH constant at 4.5, over a contact time of 400 h.

Samples collected from all sorption studies were filtered using 0.2 μm membrane filters. Aqueous arsenic concentrations in these filtrates were measured using graphite furnace atomic absorption (GAA) spectrometer (Perkin-Elmer Analyst 800) (Deaker et al., 1999).

XAS Studies

The local coordination of As(V) in the sorption complexes was studied as a function of reaction time, sorbate loading, and the presence or absence of phosphate using x-ray absorption spectroscopy (XAS). All XAS studies were conducted on beamline X11B at National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, where the maximum storage ring beam energy was 2.8 GeV with a maximum beam current of 280 mA. To compare and identify the local structure of As in the sorption complexes, XAS spectra were also collected for the following arsenic references: $\text{As}_2\text{O}_5(\text{s})$, $\text{As}_2\text{O}_3(\text{s})$, and a 10^{-1} M aqueous sodium arsenate solution at pH 4.5. Multiple scans were collected for each sample to improve signal-to-noise ratio. Details in experimental methodology and data evaluation are described in Tanwar et al. (2005).

Principal findings and significance

Sorption Studies

The results obtained from the isotherm studies show (Figure 1a) a linear correlation between the moles of As(V) sorbed g^{-1} HAO and the bulk aqueous As(V) concentration at lower concentrations. At higher concentrations, the isotherm approaches a plateau, which represents saturation of sorption sites available on the external surface and as well as on the macropore walls of HAO. The isotherm was modeled using the single site Langmuir isotherm model. This model assumes one type of reaction sites, monolayer coverage, and no change in affinity with sorption density (Fogler, 2002).

As shown in Figure 1a, this model satisfactorily fits experimental data. The estimated maximum sorption capacity (C_i) of HAO for As(V) is 1.9×10^{-3} mol g^{-1} HAO (within 21% standard deviation) and the equilibrium constant (K) is approximately 4.5×10^3 L mol $^{-1}$ (within 21% standard deviation). Anderson et al. (1976) reported the maximum sorption capacity for As(V) as 1.6×10^{-3} mol g^{-1} on amorphous aluminum oxide at pH 5, which is slightly lower than

that found in the present study. The higher sorption capacity achieved in the present study can be attributed to lower pH used in this study, which would result in higher net positive charge on the oxide surface, and therefore in a high apparent capacity for oxyanions such as As(V).

The isotherm experiments conducted in presence of phosphate were also modeled using the same single-site Langmuir isotherm model. For modeling this isotherm, the equilibrium constant was constrained as equal to the value estimated in single system studies; The isotherm modeling for this study is presented in Figure 1b. The modeling results reveal that the sorption capacity for As(V) sorption on HAO is $1.6 \times 10^{-3} \text{ mol g}^{-1}$ (within 21% standard deviation) in presence of phosphate as compared to the single sorbate system, where it is approximately $1.9 \times 10^{-3} \text{ mol g}^{-1}$ (within 21% standard deviation). These results indicate that sorption capacity of HAO for As(V) decreased slightly due to presence of phosphate. However, this decrease seems insignificant if associated errors are considered.

To obtain information about the rate limiting step, long-term As(V) sorption was studied over a reaction time of 400 h, under different mass-transfer conditions. The time dependence of As(V) sorption onto HAO under two different mass transfer conditions, i.e. one time addition (TBC) and continuous supply (CIC), is presented in Figures 2a and 2b, respectively. A total of 10^{-3} moles As(V) was added to the reaction system in both TBC and CIC studies. In TBC studies, approximately $8.7 \times 10^{-4} \text{ mol As(V)}$ was sorbed g^{-1} HAO after reaction time of 4 h and no significant increase in uptake of As(V) was observed after the reaction time of 4 h until 300 h (Figure 3a).

Under similar mass transfer conditions, Arai et al. (2001) observed an increase in As(V) uptake from 1.9×10^{-4} to $2.0 \times 10^{-4} \text{ mol g}^{-1} \gamma\text{-Al}_2\text{O}_3$ with increase in reaction time from 72-8760 h. Likewise, Fuller et al. (1993) observed rapid uptake of As(V) on ferrihydrite within the first 4 h followed by a very slow uptake till a reaction time of 200 h. Although the magnitude of increased uptake in these studies appears insignificant, it indicates that the process following rapid initial adsorption is very slow and might take months to years to reach equilibrium. Therefore, it is difficult to assess the contribution of such slow processes under these conditions.

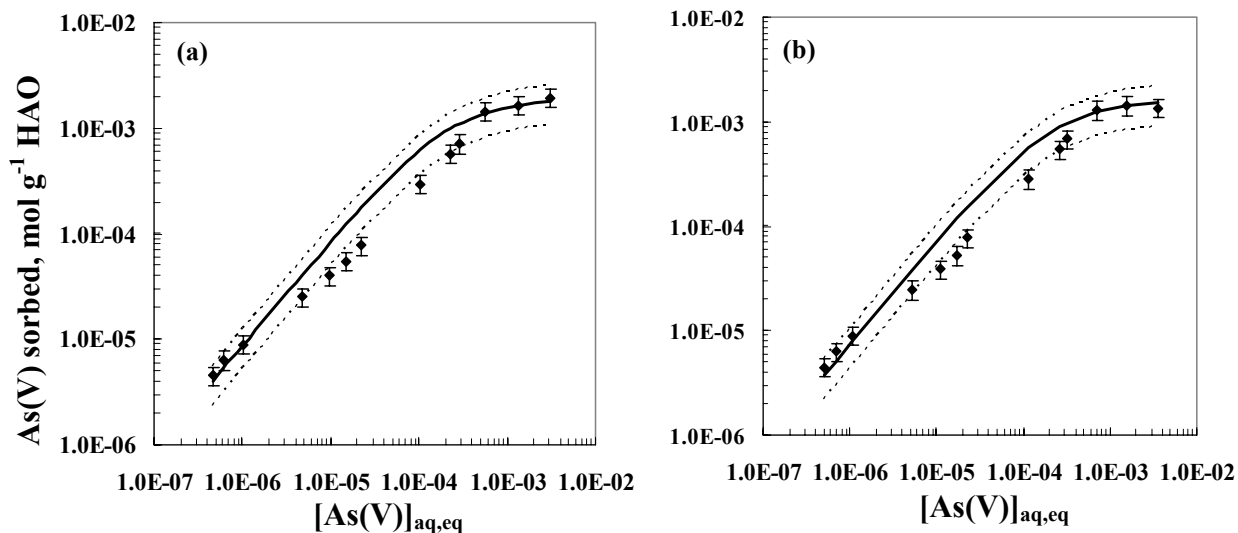


Figure 1. Arsenate adsorption isotherms conducted at 25°C, pH 4.5, I.S. 10⁻² M. Solid lines represent the single site Langmuir mode, dashed lines show the associated errors of ± 2 SD

(a) in absence of phosphate;

(b) in presence of phosphate in equimolar amount with As(V).

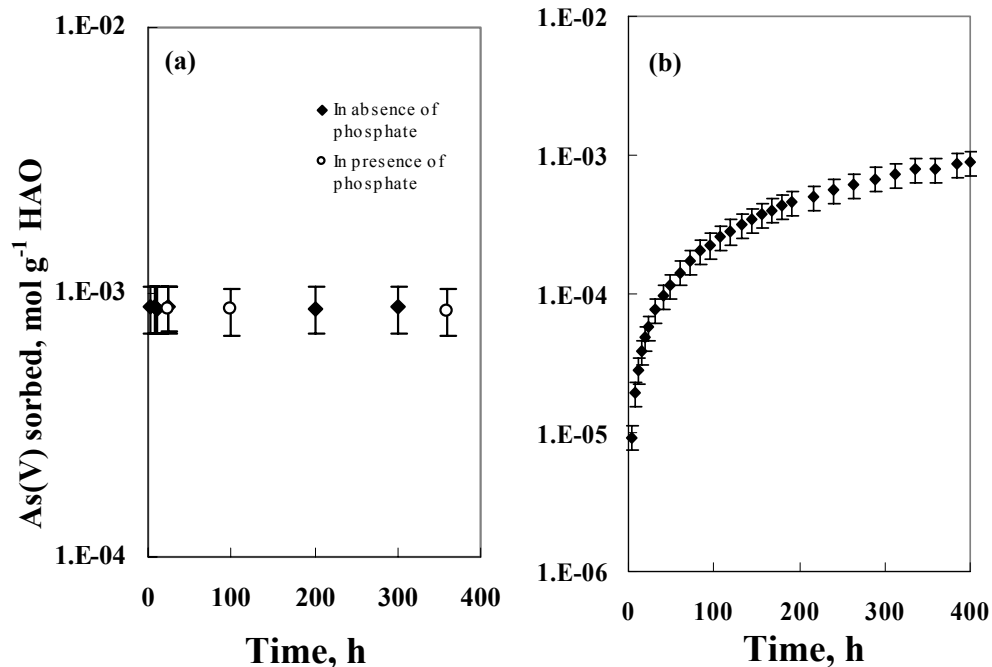


Figure 2. Long-term kinetic studies of As(V) sorption on HAO (pH 4.5, I.S. 10⁻² M)
 (a) Traditional boundary conditions, in absence and presence of equimolar phosphate
 (b) Continuous influx conditions, 10⁻⁵ M As(V) supplied every 4 h.

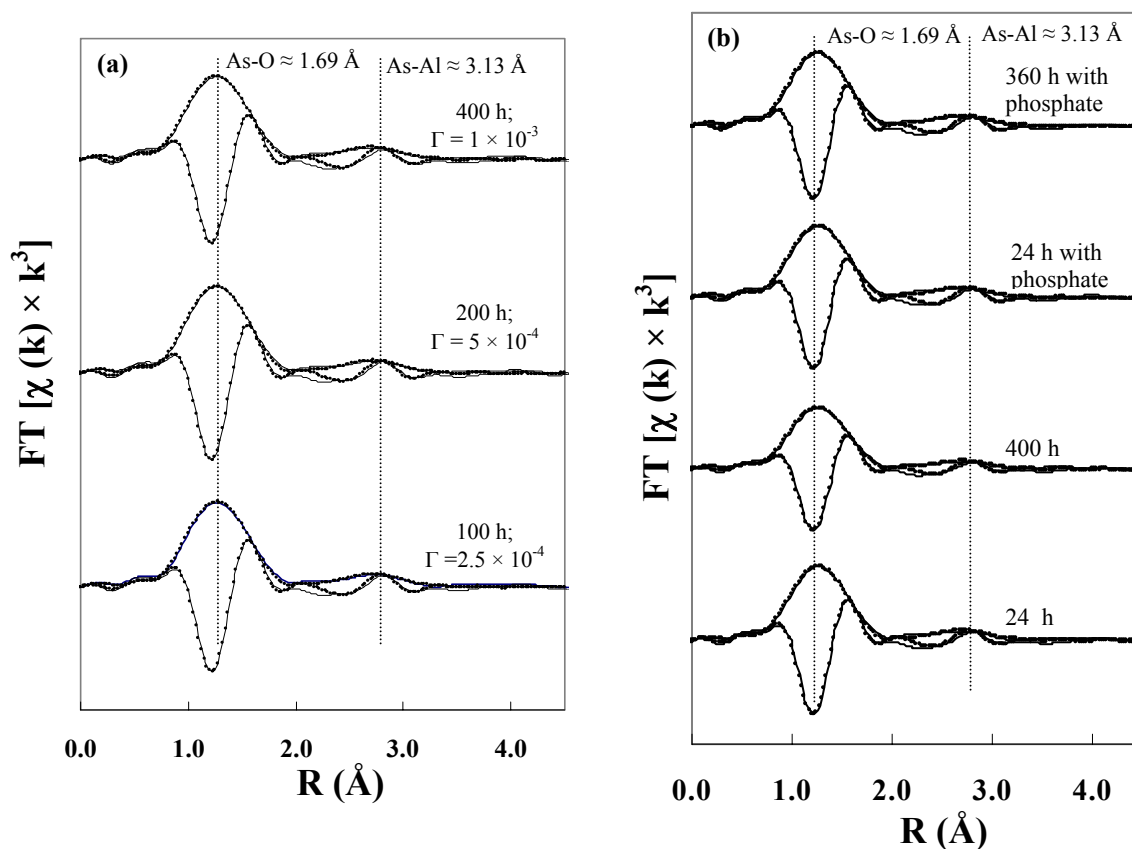


Figure 3. Fourier transforms (solid lines) fitted with aluminum substituted scorodite (dotted lines) from 0.60-3.30 Å. Γ - total sorbate dosage, moles As(V) g⁻¹ HAO
 (a) continuous influx conditions ,
 (b) traditional boundary conditions.

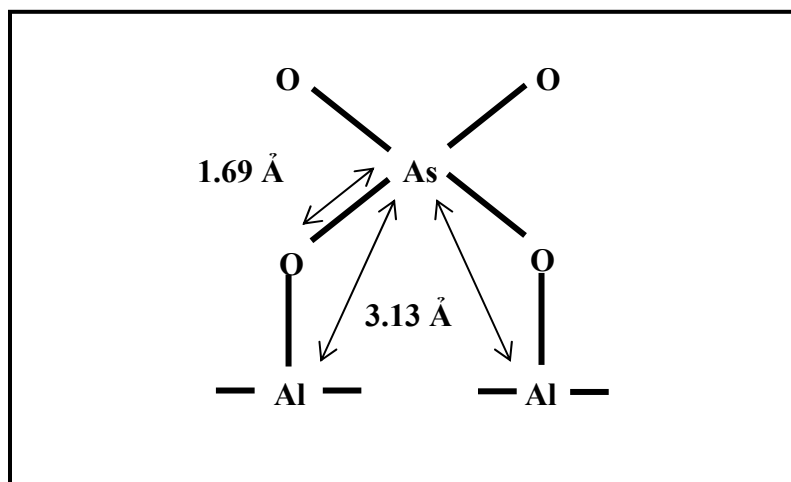


Figure 4 Local structure of As(V)-HAO sorption complexes based on XAS results. As-O \approx 1.69 Å and As-Al \approx 3.13 Å.

To maintain a continuous concentration gradient of As(V), continuous influx condition (CIC) studies were conducted, where 10^{-5} M of As(V) were added every 4 h to the reaction system, over a reaction time of 400 h. Unlike TBC studies, the results of this study reveal that there was a rapid uptake until a reaction time of 24 h, and a slow but continuous uptake until the reaction time of 400 h (Figure 2b). Additionally, a slightly higher uptake of As(V) (8.9×10^{-4} mol As(V) g⁻¹ HAO) was observed in CIC studies as compared to TBC studies. The final concentration of As(V) in bulk solution was approximately 1.1×10^{-4} M at the end of 400 h. This difference can be qualitatively explained in terms of maintaining a driving force for diffusion and the porous nature of HAO. In TBC studies, where the sorbate is supplied only once, the initial sorption is predominantly on surface sites. With increase in reaction time, the sorbate may start migrating to pore walls of HAO. This migration would vacate few external reaction sites, where further uptake of sorbate is possible. But this process is likely to be slow and therefore, no significant increase in uptake due to diffusion can be detected within the time frame of this study. In comparison, sorbate was continuously re-supplied in CIC studies. The re-supplied sorbate is likely to occupy the external surface sites that are previously unoccupied as well as the sites that are vacated due to migration of sorbate to pore walls of HAO. In other words, the total sorption in CIC studies has contribution from sorption to external sites as well as uptake into pore walls due to intra-particle diffusion. Thus, the results of the present study suggest that intra-particle diffusion could be the predominant rate limiting step in case of long-term studies, which further indicates that intra-particle diffusion may be an important process that controls the long-term fate of As(V) in environment.

Another important factor that can impact sorption of As(V) is the presence of competing oxyanions. The sorption studies conducted in presence of phosphate revealed that an equimolar amount of phosphate did not affect As(V) sorption over a reaction time of 360 h (Fig 2a). In comparison, Jain et al. (2000) suggested that the presence of an equimolar amount of phosphate reduced the sorption of As(V) by 0.7 % at pH 4 on ferrihydrite; however the associated errors were not reported. Therefore, this small change is likely insignificant. In contrast, Liu et al. (2001) reported that the sorption capacity of goethite for As(V) decreased from 1.8×10^{-4} to 1.1×10^{-4} mol g⁻¹ due to the presence of an equimolar amount of phosphate at pH 4.0. However, the results of the present study suggest that the effect of an equimolar amount of phosphate on arsenate sorption on HAO is insignificant at pH 4.5.

XAS Studies

The XAS results are used to determine the nature of As(V)-HAO sorption complexation reactions as a function of contact time, sorbate loadings, and different mass transfer conditions (TBC and CIC). The fourier transforms and fits are presented in Figures 3a and 3b. For all sorption samples, the best fit first shell suggested approximately four oxygen atoms at an average radial distance of 1.69 ± 0.02 Å. Similar As-O distances were observed with other sorbents.

The best fits revealed that the second shell has two Al atoms at an average radial distance of 3.13 ± 0.05 Å. These As-Al distances and coordination numbers do not resemble Al-substituted scorodite, which has four Al in second shell with distances ranging from 3.34-3.38 Å. Thus, the precipitation or solid solution resulting in formation of AlAsO_4 can be considered insignificant. Furthermore, inclusion of As and/or O in the second shell of As(V) sorbed onto HAO, in absence or presence of Al atoms, did not provide reasonable fits. This suggests that there are no As-As interactions in the sorption complexes. The lack of these interactions validates the assumption of the Langmuir isotherm that there are no sorbate-sorbate interactions. The coordination numbers and bond distances obtained from EXAFS results of this study suggest that As(V) appears to react with HAO to predominantly form bidentate inner sphere complexes (Figure 4), where there is no interaction between the sorbed arsenate species.

The long-term stability of these sorption complexes plays an important role in determining the predominant reaction mechanism. Interestingly, the local coordination of As(V) sorbed onto HAO, under traditional as well as constant boundary conditions, did not change between 24 and 400 h of contact time. In the present study, the coordination of the sorption complexes did not vary with sorbate/sorbent ratios, over three orders of magnitude of sorbate concentration (10^{-4} - 10^{-2} M As(V)), under either of the two (one time addition and continuous supply of As(V)) reaction conditions. Since no change in sorption mechanism occurred, one can reasonably attribute the continued uptake of arsenate by HAO to the slow migration of As(V) inside the micro- and/or nano-pores of these oxides, where the sorption sites are apparently similar to those located on the external surfaces as well on the macropore walls of HAO.

The local coordination and structure of sorption samples prepared in absence and presence of phosphate show a strong resemblance. This similarity suggests that equimolar amounts of phosphate has little to no influence on As(V)-HAO reaction mechanisms over a reaction time of 360 h at pH 4.5. Thus, these spectroscopic results validate the modeling of binary system isotherms using a Langmuir isotherm model with the equilibrium constant estimated from single system studies.

Conclusions

Overall, the macroscopic and spectroscopic analyses conducted in this study provide a few important conclusions. Most importantly, As(V) chemisorbs onto HAO, via one average reaction mechanism over a wide range of sorbate/sorbent ratios resulting in bidentate inner-sphere complexes.

This, in turn, justifies fitting of As(V)-HAO adsorption isotherms with a single-site Langmuir isotherm model to obtain a unique equilibrium constant and a maximum sorption capacity at constant pH.

Importantly, the sorption capacity of HAO for As(V) was not affected by the presence of phosphate in equimolar amount with As(V). Additionally, for a given set of sorbate/sorbent ratio, pH, and temperature, the structure of As(V)-HAO complexes does

not vary with time and/or presence other background oxyanions, such as phosphate, which is indicative of their chemical stability.

Furthermore, since no change in mechanism occurred over time, the slow and continuous uptake of As(V) by microporous HAO for continuous As supply can be attributed to intraparticle diffusion, where the sorption reaction mechanism along the micro- and nano-pore walls is similar to the one on the external surface. Thus, microporous oxyhydroxides of aluminum are much larger sinks for oxyanions, such as As(V), than presently understood.

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